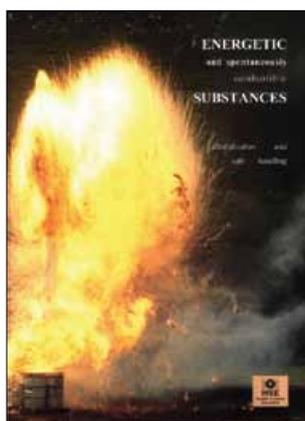


Energetic and spontaneously combustible substances

Identification and safe handling



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ISBN 978 0 7176 0893 5
Price £7.50

The aim of this guide is to assist chemical manufacturers and warehouse managers in identifying energetic and spontaneously combustible substances. It provides advice on the storage, manufacture and use of these substances and gives guidance on the practical application of the law and ways to comply with health and safety legal requirements.

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First published 1995

ISBN 978 0 7176 0893 5

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Preface

The main aim of this booklet is to provide information to assist chemical manufacturers and warehouse managers with the identification of energetic and spontaneously combustible substances. It also provides guidance on the storage, manufacture and use of these substances. Organisations or associations may wish to use it as a basis for more specific guidance for their own members.

In addition, this booklet provides advice on the practical application of the law, and gives guidance on ways of complying with legal requirements. Variations from the recommendations, guidance and advice given may be appropriate to suit individual circumstances or where alternative means of achieving an adequate standard of safety are provided.

Introduction



Figure 1 During cleaning of residue from a distillation vessel used to recover an aromatic nitro compound, an incandescent flame erupted from the vessel scorching a path through a nearby building before hitting a large office block. Two employees were killed instantly and three others, including a young office worker, died from their injuries several days after the incident. The company was prosecuted for an alleged breach of section 2(1) of the Health and Safety at Work etc Act 1974 and fined £250 000, with costs of £150 000 awarded to HSE

Scope

1 This booklet contains advice on substances that produce energy, mainly in the form of heat, by self-reaction or reaction with air or moisture. Such substances include those which will be termed 'energetic' and these are discussed in paragraphs 4-73. Some examples of energetic substances are included in Appendix 1.

2 Paragraphs 74-102 provide information about spontaneously combustible substances and Appendix 2 contains examples of general types. However, the guidance on identification and labelling of energetic substances is also relevant, and for some spontaneously combustible substances the section on control of energetic substances may also be relevant.

3 The scope of this guidance does not include substances that are manufactured with a view to produce a practical effect by explosion, or a pyrotechnic effect and other substances subject to control under the Explosives Act 1875. Advice on these can be obtained from HM Explosives Inspectorate, Magdalen House, Bootle, Merseyside L20 3QZ. However, the guidance may be useful to those who manufacture other explosive substances subject to the Classification and Labelling of Explosives Regulations 1983.

Background

4 Recently, a small but significant number of accidents have involved energetic substances. Many of the incidents arose due to a failure to appreciate the energetic properties of the substances in use. Some typical incidents are summarised as case histories at appropriate places in the text.

5 The HSE publication *Storage of packaged dangerous substances*¹ provides general guidance on the storage of dangerous goods. It emphasises the need for good organisational arrangements, including store management and training of employees. It gives general guidelines on how to segregate dangerous goods by UN class but points out that some materials may require special storage conditions. It also contains guidance on the provision of information to the emergency services.



Figure 2 In 1992 a major fire in a warehouse demonstrated the consequences of accidentally overheating a stored energetic substance.² The incident was made worse because the substance was also stored with incompatible substances. In that incident an energetic substance was stored too close to a steam heating pipe. The heat from the pipe caused the substance to decompose with the result that the drum burst and the substance was spread around the store. The substance settled on an oxidising agent stored in the same room and the resulting mixture ignited. The ensuing fire destroyed the warehouse

Legislation

6 The Health and Safety at Work etc Act 1974 is concerned with securing the health, safety and welfare of people at work and with protecting people who are not at work from risks to their health and safety arising from work activities. Section 2 of the Act places general duties on employers and extends those duties to include among other things:

- (a) the provision and maintenance of plant and systems of work that are, so far as is reasonably practicable, safe and without risks to health;
- (b) arrangements for ensuring, so far as is reasonably practicable, safety and absence of risks to health in connection with the use, handling, storage and transport of articles and substances.

7 The Management of Health and Safety at Work Regulations 1992 include a requirement that all employers and self-employed people assess the risks to workers and any others who may be affected by their undertaking. An assessment will need to include the manufacture, storage and use of energetic substances on site. An Approved Code of Practice contains further information on risk assessment.³

8 The Provision and Use of Work Equipment Regulations 1992 include requirements covering selection of suitable equipment, maintenance, information, instruction and training. These Regulations are relevant to the selection of equipment for process plant for handling energetic substances. Guidance on the Regulations is available.⁴

9 The Workplace (Health, Safety and Welfare) Regulations 1992 require that the workplace, and the equipment, devices and systems mentioned in the Regulations shall be maintained in an efficient state, in efficient working order and in good repair. These Regulations are therefore relevant to places and equipment where energetic substances are used. Further information is contained in an Approved Code of Practice.⁵

10 The Safety Signs and Signals Regulations⁶ contain requirements for the provision of signs to indicate the presence of hazards, including dangerous substances, where risks have been identified and have not been prevented or adequately controlled by other means.

11 Certain energetic substances may also be highly flammable liquids as defined in the Highly Flammable Liquids and Liquefied Petroleum Gases Regulations 1972.⁷ These Regulations prohibit, in premises to which the Factories Act 1961 applies, the use of any equipment or other means which could ignite flammable vapours in an area where it could reasonably be foreseen that an accumulation of such vapours might occur. The Electricity at Work Regulations 1989⁸ require electrical equipment which is exposed to any flammable or explosive substance to be constructed or protected so as to prevent danger.

12 Legislation relevant to classification, packaging and labelling of dangerous substances for carriage and supply is described in paragraphs 21 and 31.

13 The Pressure Systems and Transportable Gas Containers Regulations 1989⁹ may apply where substances are contained in closed vessels and there is a risk of overpressurisation.

14 Other Regulations, which may be relevant to energetic substances depending on the quantity, are described further in *Storage of packaged dangerous substances*¹ and include:

- Control of Industrial Major Accident Hazards Regulations 1984 (CIMAH);
- Control of Substances Hazardous to Health Regulations 1994 (COSHH);
- Notification of Installations Handling Hazardous Substances Regulations 1982 (NIHHS);
- Dangerous Substances (Notification and Marking of Sites) Regulations 1990.



Figure 3 Musk xylene detonation following initiation by 200 g of high explosive

Properties

15 Chemical reactions and other industrial processes may use or produce substances with energetic (energy releasing) properties. Energetic substances may be:

- (a) unstable at or below normal room temperatures;
- (b) stable at normal room temperatures but react with air or moisture, or;
- (c) stable at normal room temperatures but decompose on heating, possibly after a prolonged time.

16 In this booklet, energetic substances are considered to be substances which because of their chemical structure are capable of undergoing rapid exothermic decomposition, or polymerisation. When an energetic substance decomposes it can result in a fire, or an explosion caused by a deflagration or a detonation. A deflagration is the propagation of a reaction at a rate slower than the velocity of sound in the substance. In a detonation the reaction front travels faster than sound and the effects are usually more devastating, particularly if the substance is confined. Confinement also increases the rate of a deflagration and may lead to a point where there is a transition from deflagration to detonation. Confinement may occur in strong containers, inadequately vented containers or large piles and stacks. Figures 3 and 4 show substances undergoing decomposition.

17 Energetic substances and their decomposition products may also be toxic, corrosive or irritant. The COSHH Regulations¹⁰ require an assessment to be made of the risks to health created by work involving substances hazardous to health, and where necessary suitable control measures may be required to prevent or reduce exposure.



Figure 4 Alcohol wetted nitrocellulose undergoing a deflagration following an initiation by a pyrotechnic device

Identification

Assessment

18 There is no simple way to determine whether a substance has energetic properties. However, all chemicals used on site should be assessed to determine whether they may have energetic properties. The following methods may be used and are summarised diagrammatically in Figure 5.

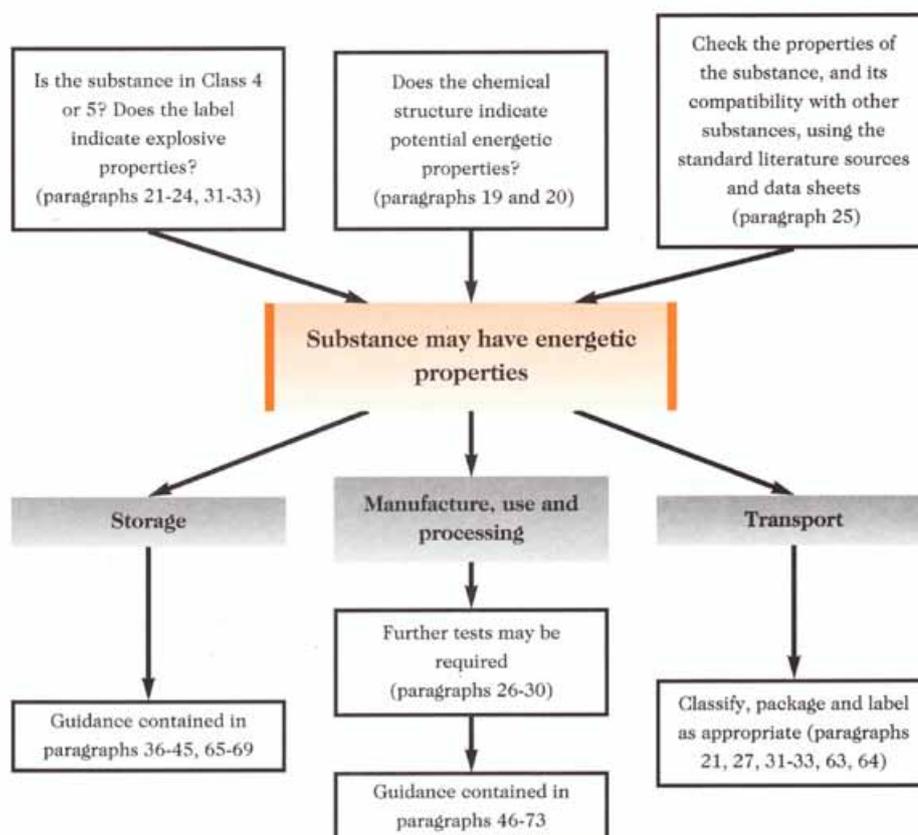


Figure 5 Identification of energetic substances

The amount of additional information required on a particular substance will depend on the magnitude of the risks identified during initial screening and the circumstances under which the substance will be handled. The following scheme summarises the questions that will need to be asked and indicates where to find guidance.

Chemical structure

19 Certain chemical groups confer on a molecule a high energy of decomposition. When this energy is released, it can result in a deflagration or a detonation depending, among other conditions, on the amount of confinement. Compounds with the following chemical groups, for example, can decompose violently:

<i>aliphatic azo-compounds</i>	(-C-N=N-C-)
<i>organic azides</i>	(-C-N ₃)
<i>diazonium salts</i>	(-CN ₂ +Z ⁻)
<i>N-nitroso compounds</i>	(>N-N=O)
<i>aromatic sulphohydrazides</i>	(-SO ₂ -NHNH ₂)
<i>peroxides</i>	(-O-O-)
<i>nitro compounds</i>	(-NO ₂)
<i>hydrazides</i>	(R-NH-NHR)

Energetic intermediates may also be produced during a chemical reaction or as a result of deterioration over time.

20 Where oxidising groups such as nitrate, peroxide or chlorate are present, the oxygen balance may be used to assess the hazard potential. For a molecule C_xH_yO_z (where other atoms are ignored), the oxygen balance is:

$$\frac{-1600(2x + y/2 - z)}{\text{molecular weight}}$$

Any result more positive than -200 indicates that the substance may have explosive properties and should be subjected to more screening tests.

Classification for carriage and supply

21 Dangerous goods for carriage by road or rail should have been classified using the method contained in the Carriage of Dangerous Goods by Road and Rail (Classification, Packaging and Labelling) Regulations 1994 (CDGCPL).¹¹ The method follows the UN *Recommendations on the transport of dangerous goods* (UN orange book)¹² in which a substance is classified according to its **principal** hazard into one of nine classes. For example toluene, a highly flammable liquid that is commonly used as a solvent, is in Class 3 and must have the appropriate label attached. Dangerous goods for **supply** should have been classified in a similar way under the Chemicals (Hazard Information and Packaging for Supply) Regulations 1994 (CHIP 2).¹³ Guidance on classification is available¹⁴ and the physico-chemical tests required for classification of new substances are described in an Approved Code of Practice.¹⁵ Further information on packaging and labelling requirements is contained in paragraphs 31-33 and 63 and 64.

22 Of the energetic substances that have been classified under the UN method, most are in the following classes:

- (a) Class 4 includes flammable solids and unstable substances and Class 5 contains oxidisers (Division 5.1) and organic peroxides (Division 5.2);
- (b) guidance on Class 5 substances can be found in *Storage and use of sodium chlorate and other similar strong oxidants*¹⁶ and *The storage and handling of organic peroxides*;¹⁷
- (c) Class 1 includes substances that have been shown in tests to have particular explosive properties. Many substances of Class 1 are subject to control under the Explosives Act 1875 and are outside the scope of this guidance. The Explosives Act, as amended, requires that all explosives are **authorised** by HSE before they are supplied, and the Classification

and Labelling of Explosives Regulations 1983 require that all explosives are **classified** before they may be conveyed, kept or supplied. HSE has published a list of authorised and classified explosives¹⁸ and also *A guide to the Classification and Labelling of Explosives Regulations 1983*¹⁹ which lists examples of substances and articles of Class 1.

23 Because Class 4 contains many energetic substances it is described in more detail in Appendix 3.

24 Although it is a useful guide to the identification of energetic substances, the UN classification is only a guide because another dangerous property of an energetic substance may take precedence. For example, dinitrotoluene may explode on heating but it has been placed in Division 6.1 because of its toxicity. Similarly, isopropyl nitrate has been placed in Class 3 as a flammable liquid. Appendix 1 contains examples of energetic substances and their classifications.

Documentation and literature search

25 The labels and data sheets that accompany dangerous goods (paragraphs 31-33) may be used to identify some energetic substances. Others may be identified from a search of the literature for known instability or reactions involving the substance or analogous substances. A selection of the standard literature sources is included in the references section.²⁰⁻²³

Thermodynamic properties

26 The energy of decomposition may be used to determine the likely stability of a substance. A large negative heat of reaction suggests that the system will generate a large amount of heat, although the rate of production of that heat will be unknown since this depends on kinetic factors. The computer program CHETAH²⁴ can be used to calculate various thermodynamic parameters and thereby identify potential energetic substances.

Testing

27 The assessment methods described in paragraphs 19–26 are useful but only offer a guide to those materials that may be energetic. Substances that have been identified by screening should be tested to establish their properties and derive safe conditions for storage and use. Appropriate tests include differential scanning calorimetry (DSC), differential thermal analysis (DTA), Carius tube, Dewar calorimetry, reaction calorimetry and accelerating rate calorimetry (ARC). These tests are described in an ABPI booklet²⁵ and typical apparatus for DSC and ARC is shown in Figures 6 and 7. The classification of substances is discussed in paragraphs 21–24 and the tests used for classification for carriage and for supply are described in UN tests and criteria²⁶ and an Approved Code of Practice¹⁵ respectively.

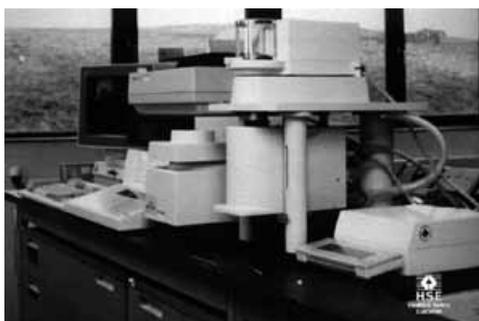


Figure 6 Sample containers (inset) for use in a differential scanning calorimeter

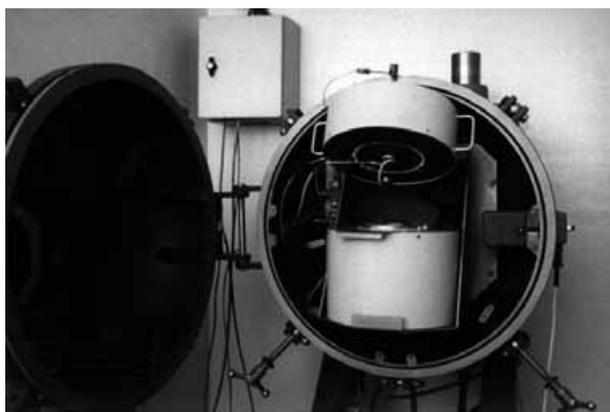


Figure 7 An accelerating rate calorimeter. The sample container usually holds 1-5 g of the test substance

28 Some of the tests are designed to give an indication of energetic properties, and may be used even where classification may not be required. Not all of the tests mentioned in paragraph 27 will be necessary for any particular substance or use, but sufficient information should be obtained to establish safe operating parameters. It is important, for the safety of the laboratory staff who carry out the tests, that sufficient information is obtained from small-scale tests, such as DSC and DTA, before substances are subjected to larger-scale tests, such as Dewar calorimetry. It will be necessary to do the tests remotely whenever there is a risk of explosion.

29 Test results will only be meaningful if they are performed on representative samples, and the effect of potential contaminants (eg water, rust, packaging materials) is evaluated. Small-scale tests, eg DSC, use milligram quantities of substance and it is therefore difficult to ensure that the sample is representative of the behaviour of the bulk material. The experimentally determined values also depend upon the rate of heating. Therefore, it is recommended that such tests are treated as screening tests and substances that show energetic behaviour in those tests are tested further. Results should be interpreted carefully by trained staff.

30 The self-accelerating decomposition temperature (SADT) is used in the classification of organic peroxides and self-reactive and related substances of Division 4.1 (see the definition in Appendix 3). The value of the SADT is obtained from experiments and represents the lowest temperature at which a self-accelerating decomposition (runaway) may occur in the package as used in transport. The SADT varies with mass of substance and the shape of the package. It is used to determine safe temperatures during transport and can offer a guide to instability in storage and use. However, if packages are closely stacked together, the SADT will be reduced since less heat can escape from the centre packages to the surrounding air. Four methods are described in the UN tests and criteria manual²⁶ for the determination of SADT, but others may be used.

Labelling

31 The CDGCPL and CHIP 2 Regulations (paragraph 21) require dangerous goods to be labelled with signs and symbols to indicate their dangerous properties. The information to be included on the labels is detailed in the Approved Lists^{27, 28} for supply and carriage that accompany the Regulations. In addition to the primary classification, some substances are required to carry labels that indicate a subsidiary hazard. The subsidiary hazard labels therefore provide further information about the substance and the 'explosive' subsidiary label warns of energetic properties.

32 The CHIP 2 Regulations require that dangerous goods should also be labelled with certain risk phrases that describe the risks that may occur during handling and use. The risk phrases are a further source of information for the assessment of energetic properties and should also be included in the data sheets required by CHIP 2.

33 All other dangerous goods, not for supply or carriage, should be adequately labelled to indicate the identity of the substance and its hazards. Sufficient information should be available to enable safe handling and storage.

Control of risks

34 Exothermic decompositions do not only occur when reactions between two or more chemicals go out of control. Neither do they only occur in chemical reactor vessels. They can occur during storage of raw materials or finished products, or during distillation, drying, transfer, milling or transport of intermediates and products. It is important therefore that all stages of production are assessed, from storage of incoming goods, through manufacture and processing, to storage of the product and disposal of waste. An HSE video²⁹ gives guidance on the control of exothermic reactions, and much of the information is also applicable to the handling and use of energetic substances. The video also shows some of the tests described in paragraph 27.

35 The risks from energetic substances can be reduced by designing plant and equipment so that inventories are minimised, and the use of less hazardous substances may be appropriate. The guidance that follows is intended to be used where the inherent risks cannot be reduced further. It is not intended as an exhaustive list of processes, and the user should consider all operations. Hazard and operability (HAZOP) studies can help to identify where problems may arise.

Operations

Storage

36 It is good practice to inspect all dangerous goods for signs of damage or decomposition upon receipt. Periodic rechecking is advisable to ensure that there has been no corrosion or build-up of heat. The frequency of checking will depend on factors such as the stability of the substance, the need for temperature control, the likelihood of containers becoming damaged and the corrosiveness of the atmosphere.

37 Some substances can be stored safely at normal temperatures but begin to decompose as the temperature increases. It is therefore unsafe to store such substances in areas that are likely to overheat due to, for example, direct sunlight. It is advisable to isolate redundant heating pipes adequately to prevent inadvertent reconnection.

38 It may be necessary to use a temperature-controlled storeroom or refrigerator and in such a circumstance it is important to monitor the temperature so that any malfunction or excessive rise in temperature can be rapidly detected and the fault remedied. There may be a risk associated with storage at too low a temperature if the energetic substance can separate from a diluent by, for example, crystallisation. It is important to know how to safely dispose of small quantities of chemicals which can no longer be kept safely. Advice on disposal of chemicals may be obtained from the supplier and can be kept readily available for use in emergencies.

A small glass bottle containing 100 g of nitrosomethylurea warmed up and exploded after it was removed from a broken refrigerator. Fortunately, there was nobody in the laboratory at the time of the explosion.

39 The temperature at which a decomposition begins may be lowered by the presence of other substances. Therefore it is not advisable to store energetic substances with other materials where there is the possibility of contamination or reaction in a fire.

40 Some substances, after prolonged storage, react with oxygen in the air to produce energetic substances. For example, some ethers can form peroxides on standing. To minimise the formation of peroxides the reagent may be stored in an inert atmosphere. However, it is advisable to test old stocks of ethers for the presence of peroxides.

A bottle of sodium amide exploded and ejected caustic materials which caused chemical burns to a laboratory assistant. The chemical had been exposed to air and stored for several years, and during this time explosive decomposition products had formed.

41 It is dangerous to store energetic substances with substances that are likely to increase the danger in a fire, eg flammable liquids, oxidisers.

42 General precautions to minimise the risk of fire and control ignition sources in storage areas are described in *Storage of packaged dangerous substances*.¹

43 In general, water is the preferred fire-extinguishing medium because it has the necessary cooling capacity to remove the heat of decomposition. However, water and water-containing foam extinguishers are inappropriate in areas that contain substances that are dangerous when wet. It is not advisable to store such substances with other combustible materials for which water is the best extinguishing medium.

44 It is advisable to consult the fire brigade to ensure that adequate supplies of water are available for fire-fighting. During some major incidents contaminated water from fire-fighting has entered water courses where it has resulted in significant environmental concern (Figure 8). Measures to avoid or minimise problems from fire water run-off include segregation of chemicals with high eco-toxicity and containment of run-off water. The amount of water needed to extinguish a fire can be minimised if the fire is detected and tackled at an early stage by, for example, early fire detection and/or automatic sprinkler systems.



Figure 8 Problems can arise from water used for fire-fighting

45 Other dangerous goods may react violently with the contents of other fire extinguishers, for example carbon dioxide or halons. It is important to use fire extinguishers that are compatible with all dangerous goods stored. Data sheets are an important source of information about suitable methods of fire-fighting. It is advisable to discuss fire-fighting requirements with the fire authority.

Transfer

46 It is recommended that pipework is installed so that it self-drains effectively. To clear the line of energetic substances which may self-heat the line can be flushed with a suitable solvent, air or inert gas, as appropriate.

When a vessel was drained, acidified dinitrotoluene became trapped in a horizontal section of pipeline. The line was trace heated with steam above the safe temperature for the mixture. It was also lagged and the valves at each end were closed so that the substance was confined. Self-reaction began and resulted in an explosion.

47 A decomposition could result if solutions that contain energetic substances are allowed to dry out. This is particularly dangerous where wetted desensitised explosives are processed. Typical places where solutions can concentrate are: at the ends of open pipes or hoses; around bottle stoppers; in leaking valves; where a spillage has not been cleaned up; and at leaking pumping equipment. It is therefore important that there are appropriate measures to deal with spillage quickly and safely, and that pipes are cleaned or capped.

Silver fulminate, a friction sensitive substance, exploded as it was being scraped into sample containers during an illicit preparation. The research student who was attempting the preparation received injuries to his hands, face, arms and eyes.



Water wet nitrogen triiodide was stored in a cupboard overnight. It dried out and exploded when an employee was cleaning the cupboard. She suffered pain and deafness for three days

48 Some explosives of UN Class 1 are desensitised with water, alcohol or other inert material and are classified in Division 4.1. It is important to ensure that these substances do not dry out since they may explode during subsequent handling.

49 It may be necessary to consider whether energetic materials can become deposited in pumps or valves since some decompositions may be initiated by self-heating of deposits or by the friction generated when a pump or valve is operated. Specially designed equipment may be required.

Processing

50 Care is required in the design of process-plant equipment to ensure that components of the equipment can not produce sufficient heat to begin a decomposition. Similarly, it is important to minimise the risk of initiation of a decomposition due to friction.

51 Despite the presence of energetic substances during some chemical reactions it does not necessarily follow that there will always be an explosion. As a result, preparative methods described in the scientific literature may not always indicate that a decomposition could occur. If the assessment methods described in this booklet suggest that energetic materials could be present, precautions may be necessary despite the lack of indication of a risk in the reported preparative method.

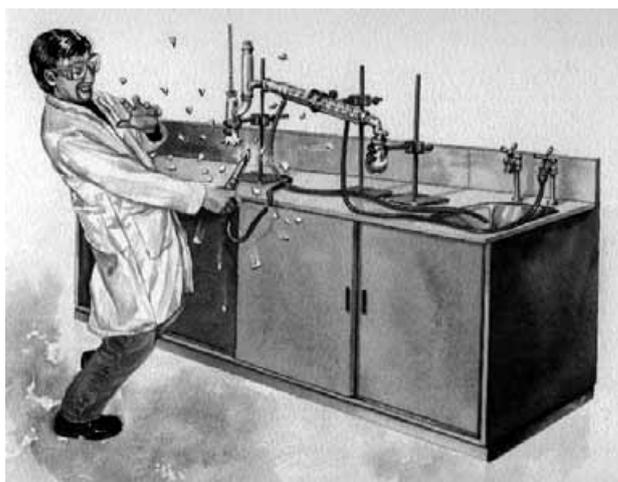
52 It is important to ensure that equipment has been cleaned adequately to remove contaminants which may lower the temperature at which a decomposition may occur.

A small amount of an impure organic peroxide decomposed violently in an 18 inch diameter glass separator. The resulting vapour cloud ignited on a shattered flameproof light fitting.

53 It is important that catalysts and other self-heating substances are not drawn into air-extraction systems where they could lead to fire spread in ductwork and collection systems or ignition of flammable vapours.

Distillation

54 Explosions have occurred when energetic substances were being purified by distillation. The product itself may be unstable, or by-products formed in the still may decompose or lower the SADT of the product. It is unsafe to handle thermally unstable substances without a proper understanding of their safe temperature limits and an effective means of monitoring these limits. Similarly, an understanding of the thermal stability of by-products may be as important as it is for the main product. Detailed analytical work is likely to be required before the substances are used on a large scale, and before an energetic substance is distilled it is important that it has been tested to establish the stability of the product and residues. During the distillation it is important to monitor the temperature accurately and therefore the temperature probe needs to be located so that it remains immersed in the liquid as the level falls. It is advisable to fit an alarm that will warn the operator if the liquid falls below a set level, and switch off the heater automatically.



A research student was distilling a small quantity of a new organic azide against the advice of his supervisor when it exploded. The student received minor injuries from broken glass

An energetic substance had been distilled without incident for 10 years until the process was scaled up to a 300 gallon reactor. During the distillation the level in the reactor fell below the temperature probe. The batch overheated until it decomposed explosively. Fortunately the injuries sustained from flying glass were minor.

A mixture of nitrobenzaldehyde isomers was being fractionally distilled when it began to self-react exothermically with evolution of gas. Evacuation of the building began but an employee who was working in another part of the building was present when the still exploded. The employee was dazed and had to be freed from the debris.

55 Residues from distillations may decompose during subsequent storage. Therefore it may be necessary to test them to establish how long they can be stored safely and at what temperature.

A 2200 litre solvent recovery vessel exploded 2 hours after isopropanol had been distilled from residual reaction liquors and heating had been discontinued. Both the product and raw material from the chemical reaction contained nitro-compounds that could self-react exothermically but this had not been appreciated during the HAZOP.

56 Because substances react more rapidly with air at higher temperatures, it is generally important to cool vacuum distillation stills before releasing the vacuum by introduction of air, or preferably nitrogen.

57 In continuously operated stills, or batch stills which are not cleaned between batches, residues or deposits in the still may contain energetic by-products which can increase in concentration over time. It will be necessary to establish a suitable frequency of cleaning for the still, and a safe system for removing residues. The cleaning frequency for the still may be established from tests performed on the actual residues. Suitable tests are described in paragraphs 27–30. It is important to note that solid residues may form on heating elements with the result that local overheating and decomposition could occur which could then spread to the rest of the still contents.

Drying

58 Guidance is available on the prevention of fires and explosions in the drying of solids.³⁰ The following paragraphs extend that advice.

59 Some energetic substances may be safely dried at an elevated temperature for a specified period of time. However, after a prolonged period at that temperature self-heating may progress to the point where a runaway decomposition may occur. It is important to specify and adhere to maximum drying times. It may be unsafe to store substances in dryers at elevated temperatures and for extended periods while waiting for analytical results, or for other equipment to become available.

A poultry feed additive had been left in a closed dryer for 27 hours after the drying process had been completed. The insulation of the dryer maintained the temperature between 120-130°C and under those conditions the chemical began to decompose, with the evolution of heat causing self-accelerating decomposition which led to an explosion.

60 It is also important to specify the maximum temperature permitted in the drying medium. Lower drying temperatures may be achieved by the use of vacuum. However, it may not be appropriate to dry certain energetic materials in a vacuum dryer because this type of dryer has a heavy sealed construction and therefore a serious explosion could occur. Where necessary for safety, alarms should be fitted to warn of excessive rises in temperature or loss of vacuum.

61 It is generally advisable to cool substances before they are removed from the dryer. Similarly, it is advisable to allow those substances that undergo self-heating in air at elevated temperatures to cool before air is admitted to the dryer.

Milling and sieving

62 Frictional heating of certain energetic substances could lead to an explosive decomposition. Tests can determine the sensitivity of a substance to friction and it may be necessary to prohibit these operations. Alternatively, it may be possible to use an inert phlegmatiser. Where it is desirable to remove tramp metal, which may otherwise initiate a decomposition, due to sparks or frictional heating, magnetic separators may be suitable. In addition to the risk of decomposition, there may be the risk that a dust explosion could occur during milling or sieving of some substances. Guidance on dust explosions is available.³¹

Dinitropentosamine decomposed in a 2-roll mill while it was being mixed with a rubber compound. The mill was destroyed. The incident probably occurred due to contamination or because overheated bearings caused local heating of the mixture.

Packaging

63 Energetic substances should be packaged and labelled correctly for carriage and supply. The series of UN tests²⁶ have been designed to establish the energetic properties of the substance relevant to transport and define the type of packaging required to minimise the consequences of any accident during transport.

64 In a fire many energetic substances will explode with greater force if confined. Consequently, they may be packaged in fibreboard kegs or steel drums fitted with lids designed to relieve at a set pressure. It is unwise to repackage these substances if that would increase confinement.

Storage and disposal of waste

65 It is important that the storage considerations applied to raw materials, intermediates and finished products are also applied to waste products. It is important to consider the procedures on the plant to prevent the mixing of incompatible waste and to ensure safe disposal on or off site.

66 Chemical reactions may produce waste that contains energetic by-products. These by-products may begin to self-heat and an explosion could result. Reaction assessments should include a consideration of the products formed in the reaction, and testing may be necessary. It is desirable to destroy or otherwise deactivate energetic by-products as soon as possible, and before they leave the site.

67 It is recommended that waste is stored in closed containers and removed regularly to minimise the amount stored. It is important to inspect containers regularly for signs of corrosion or self-heating.

68 It is important to consider the disposal of cleaning rags, etc which may be contaminated with substances that could self-heat.

69 Some substances can produce energetic by-products by a reaction with their container or other materials that they come into contact with. For example, sodium azide can react with lead drains to produce lead azide which can explode. Acetylene can produce explosive acetylides with copper, and certain other metals and alloys.

Filtration

70 To minimise reaction with air, some catalysts and other air-reactive materials should not be allowed to dry out on filter beds and air should not be drawn through them.

A perester was left in a filter for several hours and its temperature increased by self-reaction until it decomposed.

Inhibitors

71 Some energetic substances contain stabilisers or inhibitors that prevent reaction of the compound with air or itself. Chemicals used in the manufacture of polymers often contain additives to prevent uncontrolled polymerisation during storage. It is important that the concentration of the inhibitor does not fall below the level that is effective. Inhibitor concentration may fall by one of the following mechanisms:

- (a) crystallisation of the inhibitor from the bulk solution, particularly at low temperatures;
- (b) evaporation of a volatile inhibitor when a container is not adequately sealed or if the process temperature is too high;
- (c) contamination with for example acid, base or metals could neutralise the inhibitor;
- (d) antioxidants could be rendered ineffective if exposed to too much air, although some inhibitors require air, in small quantities, to be most effective;
- (e) removal of the inhibitor during purification processes such as crystallisation or distillation;
- (f) creation of local concentration gradients. This can occur, for example, when a monomer melts after it has frozen.

72 Information can be obtained from the supplier to enable an assessment to be made of the need for control methods to ensure that the concentration of inhibitors is maintained at an effective level. It is important to choose a grade of the substance that has a lifetime appropriate to the likely storage time. Good stock rotation will also ensure that old stock is used up first.

After a 2.5 litre glass bottle of inhibited acrylic acid exploded, a second bottle of the same batch was found to have only 125 ppm of inhibitor whereas it should have had 200 ppm. The supplier subsequently instituted further quality control procedures.

Venting

73 Some energetic substances are too sensitive to local heating or friction to rely solely on control measures. Local heating may be particularly likely in powder handling equipment due to overheated bearings, tramp metal, friction between metal components, etc. Where practicable, explosion relief vents are recommended in these circumstances to protect personnel from the effects of an explosion. The method used to determine the size of vent required should take into consideration the maximum rate of rise of pressure as determined in small-scale experiments.³²⁻³⁵ Vents may need to be larger for a decomposition than for a dust explosion. They should discharge flame and combustion products to a safe place. However, in some circumstances vents may not be practicable due to the large size of vent required or the toxicity of the materials that would be vented. In such circumstances other protective measures might be recommended, such as secondary containment, addition of an inhibitor, dumping the contents to a safe area or effective emergency cooling.

Additional recommendations

for spontaneously combustible substances

74 Certain substances react with air or moisture to liberate heat and if the heat is generated faster than it is dissipated to the surroundings, the temperature of the substance will increase. The temperature may rise to the autoignition temperature, at which point the substance, or its products of decomposition, can inflame in the absence of a recognised ignition source. This phenomenon is called spontaneous combustion. Pyrophoric substances are a special class of spontaneously combustible substance that ignite readily in air. The UN definition is given in paragraph 6 of Appendix 3.

Identification

75 Most spontaneously combustible substances that have been classified by the UN system are in Division 4.2. However, some may be found in other classes. They include:

- (a) pyrophoric gases which are in Class 2;
- (b) some organic peroxides from Division 5.2;
- (c) some substances from Division 4.1 may also self-heat when stored in large quantities for a long time;
- (d) Division 4.3 contains substances that react with water to liberate flammable gases. Some of those substances react to liberate sufficient heat to ignite the gas;
- (e) in addition, other substances may be manufactured and used in research establishments. If they are not transported off site, they may not have been classified using the UN system.

76 Examples of spontaneously combustible substances are given in Appendix 2.

Control of risks

77 Pyrophoric substances react with air or moisture. Therefore it follows that measures to prevent fires or explosions are based on adequate containment, and exclusion of air or moisture.

78 Paragraphs 79–102 include general guidelines for safe storage, manufacture and use of spontaneously combustible substances, but more specific advice can be obtained from manufacturer's data sheets and other safety-related literature to help establish safe handling procedures and other control measures.

Storage

79 It is recommended that spontaneously combustible goods are stored separately from other dangerous goods in accordance with the guidance contained in *Storage of packaged dangerous substances*.¹ That publication also contains guidance on recommended storage buildings and the location of stores. In general, it is advisable to keep spontaneously combustible materials in a special store, away from occupied buildings. If substances are stored outdoors, weather protection may be required to prevent corrosion of containers or valves. Pyrophoric substances are stored in sealed containers under an inert atmosphere, or in some circumstances under an inert liquid. It is therefore important to maintain the integrity of the

container, and to ensure that the inert atmosphere is maintained once the container has been opened.

80 The temperature that will cause the ignition of a substance that is liable to self-heating depends on the quantity and dimensions of the material. Therefore, large amounts in hoppers or bulk containers can ignite at lower temperatures than small amounts of the same material in drums and sacks. Also material formed into a cube will ignite at a lower temperature than the same material spread out in layers. Therefore it is important to know the maximum temperature to which a particular quantity of substance can safely be exposed, the safe package size and the safe storage time. It also follows that it is necessary to assess the fire risk before self-heating substances are packed closely together or bulked into hoppers and process equipment such as dryers and blenders. The guidance for energetic substances in paragraphs 37 and 38 is generally applicable to prevent the external heating of self-heating substances during storage.

81 It is recommended that large vessels for pyrophoric liquids such as butyllithium in hexane are provided with a bund capable of containing 110% of the contents of the largest vessel. It is advisable to slope the ground so that spills flow away from the tanks. It is important that vessels are adequately separated from each other and from tanks containing other dangerous goods to prevent the escalation of any incident that may occur.

82 A code of practice from the British Compressed Gases Association³⁶ gives guidance on the storage of silane and other pyrophoric gases used in the microelectronics industry. The general principles may be applied in the manufacture and use of these gases.

Choice of reagent

83 The risks from pyrophoric substances may be reduced in some circumstances by appropriate selection of reagent, solvent and concentration. For example, different organometallic reagents vary in their reactivity with air or water, and the stability of different isomers varies depending on branching of the molecular chain. Thus t-butyllithium is more reactive than n-butyllithium. Paragraphs 84 and 85 indicate other factors that affect reactivity, and therefore selection, of reagents.

84 Lower concentrations of pyrophoric substances in organic solvents are less likely to produce sufficient heat to ignite the solvent vapour. At higher concentrations more heat is generated, thereby increasing the likelihood of spontaneous ignition.

85 Solutions of pyrophoric substances are more likely to ignite if the solvent has a low flash point. In addition, the solution may become more concentrated due to evaporation if the solvent is more volatile. The fire risk may be reduced by the use of a non-flammable solvent. It is advisable to conduct small-scale experiments to determine the most suitable choice of reagent and solvent to reduce the risks.

Purging

86 It is essential that vessels are adequately purged of air, and dried if necessary, prior to the introduction of a pyrophoric substance. An adequate supply of purge gas will be required to ensure normal operation and emergency purging.

87 It is important that the danger of asphyxiation from working in or near oxygen depleted atmospheres is appreciated.

88 The purge gas supply should preferably be from a dedicated source to avoid the possibility of back-contamination from other sources. Where this is not reasonably practicable, it is important that systems of work are in operation to prevent accidental entry of air into the purge line. It is important that the maximum

permitted level of oxygen is specified and the oxygen content monitored. The use of non-return valves at each point where the nitrogen supply can discharge into a process vessel can help to reduce the risk of contamination.

89 It is important to ensure adequate control over the pressure and flow rate of purge gas. Overpressurisation could result in damage to the vessel or pipework through which air could enter. To prevent the ingress of air, a positive pressure of inert gas needs to be maintained in the reactor vessel and associated equipment. This is usually achieved with a continuous flow of inert gas that escapes to atmosphere through a liquid-sealed 'bubbler' which is designed to prevent suck-back of liquid into the reaction mixture. It is important that the level of liquid in the bubbler is monitored regularly.

90 Overpressurisation may also occur if there is an increase in vapour pressure. This may arise if the substance or reaction mixture is overheated or if air enters the system. It may also arise if an energetic substance begins to self-heat in the absence of air. It is therefore important that equipment is designed to relieve excess pressure safely. Where the provision of relief vents is not reasonably practicable, it is important to demonstrate that the reaction is adequately controlled so that overpressurisation is unlikely to occur. It may be necessary to use protective screens or containment cells.

A batch of the pyrophoric substance trimethylindium (TMI) was being heated by an electric mantle when, due to inadequate temperature control, the temperature was increased until the substance began to decompose. The increase in pressure caused the reaction vessel to burst and release TMI which spontaneously ignited.

Transfer

91 It is important to construct pipework and flexible hoses used for transferring pyrophoric substances from materials resistant to the chemical action of the substance. It may be necessary to consider the possibility of mechanical damage, corrosion, high pressures and excessive heat. For small-scale laboratory transfers, flexible tubing such as Viton may be appropriate where damage is not reasonably foreseeable, but should be minimised. Such tubing should be resistant to the action of the substance that it will contain and should be capable of resisting any pressures likely to be encountered. It is important that pipework is regularly inspected and replaced if it becomes damaged or worn.

92 It is advisable to keep pipework as short and straight as possible, with the minimum number of connections. Joints in pipework should preferably be welded, particularly where operations are done under reduced pressure or where pyrophoric gases are used. The consequences of a leak can be minimised if joints in pipework are in well-ventilated areas. For ease of isolation, sections of connected pipework are better if separated by valves. Gaskets, seals and greases are only appropriate if they are compatible with the substances that they are likely to come in contact with and will not result in leaks. It is important that pipework is located where it is unlikely to suffer damage either in normal use or during maintenance or cleaning activities.

93 It is recommended that the whole system is pressure tested for leaks prior to the introduction of a pyrophoric substance.

94 Where syringe needles are used in small-scale transfers, it is important that their diameter is sufficient so that they do not become blocked with the particulate deposits that can often form in pyrophoric solutions. Similarly, on larger scales, it is important that valves and relief systems do not become fouled since this could result in leaks.

95 It is important to avoid sections of pipe where pyrophoric substances could become trapped. When pipelines and vessels have been emptied of pyrophoric substances, it is important to rinse them with a suitable solvent, or otherwise purge them before air is admitted. Maintenance work is one of the likeliest activities for accidentally introducing air or water into vessels containing pyrophoric or water-reactive substances. Care will therefore be required in preparing for, and carrying out, maintenance on such plant. An HSE booklet provides advice to help avoid accidents from maintenance work in the chemical industry.³⁷

Reaction with water

96 Some substances produce flammable gases when they react with water and adequate safeguards are required to prevent them from coming into contact with water. It is important that there are adequate procedures to ensure that equipment is dry before it is brought into use. Leaking water or steam pipes are dangerous unless they are repaired quickly. Pools of water are also dangerous if a water-reactive substance is spilled.

97 It is recommended that water-filled condensers are avoided if proposed chemical reactions involve water-reactive substances. If they are used, it is important that the system is designed to prevent water from entering the reaction mixture if a condenser breaks.

Protective clothing

98 Engineering controls and safe systems of work should be regarded as the primary means of reducing risks to an acceptable level. However, where the risks are not adequately controlled by these methods, operators handling pyrophoric substances should wear suitable protective clothing. Supplier's data sheets should provide advice on the equipment necessary, but where large quantities are handled it will usually be necessary to specify the use of face shields, fire resistant clothing, chemically resistant gloves and boots, and head protection. Special metallised suits are available for high risk operations. It is important that protective clothing can be removed easily in an emergency and is inspected regularly for damage. A guidance booklet on the Personal Protective Equipment Regulations 1992 contains advice on the selection, use and maintenance of personal protective equipment.³⁸

Substances liable to self-heat when stored in bulk

99 The substances described in paragraphs 20–22 of Appendix 2 do not usually ignite unless stored in bulk for a long period. Control over ignition generally involves limitation of the size of the pile, avoidance of water entering the pile and prevention of aeration of oxidisable materials. The last two controls may involve covering the pile with impervious sheeting. Where initial heating is caused by bacterial action, aeration may be desirable to reduce the activity of anaerobic bacteria and to cool the stack. It may be necessary to monitor the temperature at the centre of a stack at regular intervals if it is likely to rise to a dangerous level. The temperature at the centre of the stack may be measured by the use of a temperature probe attached to a long pole.

100 Good stock rotation will reduce the storage time and therefore minimise the temperatures achieved in some circumstances.

101 Turning over a pile will also minimise the temperature at the centre. With some materials, however, this procedure could lead to inflammation of a smouldering pocket, and a careful assessment of the risks and procedures for extinguishing fires may be necessary. In dust handling equipment, smouldering material can ignite a dust cloud. *Safe handling of combustible dusts*³¹ contains advice on the normal precautions to mitigate the effects of a dust explosion.

102 It is recommended that gangways of sufficient width are incorporated into large stacks to provide access for routine use and in emergencies.

Appendix 1

Examples of energetic and spontaneously combustible substances and UN classification

The following examples have been classified for transport (this is not an exhaustive list):

Substance	UN Classification
3-Bromopropyne	3
Butyl nitrites	3
Isopropyl nitrites	3
Nitrocellulose solution	3
Nitroethane	3
Sodium methylate (methoxide), solutions in alcohols	3
Ammonium picrate, at least 10% water	4.1
Azodiisobutyronitrile (AZDN)	4.1
Isosorbide dinitrate mixture	4.1
Sodium dinitro- σ -cresolate, wetted	4.1
Sodium picramate, wetted	4.1
Trinitrobenzene, wetted	4.1
Trinitrophenol, wetted	4.1
Urea nitrate, wetted	4.1
Butyllithium	4.2
Magnesium dithionite	4.2
Sodium methylate (methoxide), (solid)	4.2
Sodium sulphide	4.2
White phosphorus	4.2
Calcium carbide	4.3
Lithium aluminium hydride	4.3
Sodium hydride	4.3
Sodium phosphide	4.3
Ammonium nitrate	5.1
Ammonium perchlorate	5.1
Guanidine nitrate	5.1
Ammonium dinitro- σ -cresolate	6.1
Dinitrobenzenes	6.1
Dinitroanilines	6.1
Dinitro- σ -cresol	6.1
Sodium azide	6.1

Appendix 2

Types of spontaneously combustible substances

1 The following categories provide examples of the most commonly used spontaneously combustible substances. Other more specialised compounds may be encountered.

Metals

2 Finely divided metals have a large surface area available for reaction with air or moisture. Reactivity is affected by particle size, nature of the surface (eg pore size) and heat of reaction. Moisture may decrease reactivity because it aids heat conduction. However, some metals may decompose water with the evolution of heat, which then contributes to the temperature rise occurring due to autoxidation. Hydrogen can be produced and may then ignite.

3 Alloys may be more pyrophoric than their constituent metals.

4 Metals often react slowly with air so that an oxide coating is produced which inhibits further reaction. However, if natural cooling is insufficient, the metal may still ignite.

5 Metals are rarely pyrophoric in the massive state but the phenomenon has occurred with uranium, plutonium and thorium due to the build-up of heat from nuclear fission.

6 Contamination with sulphur compounds may result in the formation of pyrophoric sulphides. Several incidents have occurred when steel vessels that have contained volatile sulphur compounds have ignited.

7 Some finely divided metal oxides are capable of further reaction with oxygen and may ignite after several days of exposure to air. Examples include the lower valency state oxides of iron, manganese and uranium.

8 Many metallic catalysts for the chemical and allied industries are pyrophoric. The danger may increase if they contain flammable solvents because sufficient heat may be generated by autoxidation to ignite the solvent vapour. In this way a catalyst may be more dangerous after it has been used in a reaction and should be disposed of carefully. Rags that have been used to mop up spilled catalyst may dry out and inflame.

Pyrophoric gases

9 Pyrophoric gases are commonly used in the semiconductor industry. Examples include diborane, phosphine and silane and its derivatives. A code of practice³⁶ contains guidance on pyrophoric gases.

Water-reactive substances

10 Some substances react with water or atmospheric moisture to produce flammable gases such as hydrogen, acetylene, phosphine and ammonia. Sodium reacts violently with water and produces hydrogen. Similarly, potassium reacts with water to give hydrogen, which usually ignites.

11 Substances that liberate flammable gases on contact with water include:

- reactive metals
- borohydrides
- hydrides
- carbides
- phosphides
- lithium nitride

12 The heat generated when trimethyl phosphite reacts with water causes the low flash-point liquid to vaporise and ignite.

Organometallics

13 Organometallic compounds contain carbon-metal bonds. They may be gases (trimethyl boron), liquids (trimethyl aluminium) or solids (di-*n*-butylmagnesium).

14 Alkyl aluminium compounds are used as catalysts in the polymer industry. These compounds, and the trialkyl boranes undergo autoxidation. The degree of reactivity tends to decrease as the molecular weight is increased.

15 Dialkylmagnesium compounds (R_2Mg) and Grignard reagents ($RMgX$, where X is usually Cl) are often used as intermediates in chemical synthesis or as catalysts in some polymerisations. They can react vigorously with oxygen, but commercial preparations are stable indefinitely at room temperature and under an inert atmosphere.

16 Although organozincs are less reactive than the chemically similar organomagnesiums, they are pyrophoric.

17 Alkyl sodium and lithium compounds are often encountered in chemical synthesis and, of these, butyllithiums are the most commercially important. Butyllithiums react with atmospheric moisture and the heat generated may be sufficient to ignite flammable solvent vapours.

Phosphorus and its derivatives

18 Phosphorus is usually encountered in one of two forms: red or white. Red phosphorus is oxidised slowly in air and tends to be non-pyrophoric, although large bulk quantities have ignited due to the build-up of heat in the centre of the pile. It may also ignite due to friction. Conversely, white phosphorus ignites in air at about 35°C and is normally stored under water.

19 Some derivatives of phosphorus ignite spontaneously in air. Examples are diphosphine (P_2H_4), some halophosphines and some organophosphorus compounds.

Other materials liable to self-heat in bulk

20 Some materials normally thought of as stable natural materials can also ignite spontaneously if allowed to self-heat. There are two mechanisms involved: oxidation and bacteriological action.

21 Materials liable to undergo oxidative heating include celluloid, coal, iron pyrites, oils, plastics, sawdust, rags, stearic acid, wood, soybean products and some types of wool. The mechanism of self-heating for many of these materials is oxidation of unsaturated chemical bonds.

22 Bacteriological action (eg fermentation) may raise the temperature of some materials stored in bulk. Oxidation may then raise the temperature to the point of ignition. Moisture may increase the rate of reaction, and the incidence of fires in haystacks may be reduced by covering the stack with plastic sheets to keep the rain out. Examples of materials that may self-heat by this mechanism include straw, hay, grains, meal, sugar, and peat.

Appendix 3

UN Class 4

1 The UN classifies substances by type of hazard and Class 4 comprises the following substances.

Division 4.1: Readily combustible solids

Flammable solids

2 These are readily combustible solids, and solids that may cause fire through friction. Examples are metal powders, naphthalene and sulphur. These substances are not within the scope of this guidance unless they also possess energetic properties.

Self-reactive and related substances

3 Self-reactive substances are liable to undergo strongly exothermic decomposition even without participation of air or oxygen. Substances may be placed in this category if they have:

- (a) a heat of decomposition greater than or equal to 300 joules per gram; and
- (b) a self-accelerating decomposition temperature (SADT) less than or equal to 75°C.

4 When the temperature is raised to the SADT, heat will be produced faster than it is dissipated to the surroundings. As the temperature increases, the rate of reaction increases exponentially and an explosion could occur. Substances related to self-reactive substances have a SADT higher than 75°C. Nevertheless, they may still undergo exothermic runaway if heated to the SADT.

Desensitised explosives

5 Some explosive chemicals are wetted with water or alcohols or are diluted with other substances to suppress their explosive properties. Such chemicals include picric acid, nitrocellulose and nitroglycerine. It is important that these substances are uniformly wetted and are not allowed to dry out or otherwise become concentrated.

Division 4.2: Substances liable to spontaneous combustion

Pyrophoric substances

6 These will ignite within 5 minutes of coming in contact with air due to reaction with oxygen. Heat produced exceeds the rate of cooling until the autoignition temperature is reached.

Self-heating substances

7 These react slowly with air and when stored in large amounts ignite after periods of several hours or days. Self-heaters include activated charcoal, wet straw and seedcake.

Division 4.3: Substances which in contact with water emit flammable gases

8 These substances react with water or moist air to evolve flammable gases, which often ignite. Examples include sodium borohydride, lithium aluminium hydride, calcium carbide, metal alkyls, alkali and alkali earth metals, nitrides and phosphides, and chlorosilanes.

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Energetic Substances

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Spontaneously combustible substances: pyrophoric substances: high hazard. 4.2B. Spontaneously combustible substances: self-heating substances: medium hazard. 4.2C. Spontaneously combustible substances: self-heating substances: low hazard. 4.3A. Solids that emit flammable gas when in contact with water: high hazard.